



US006171994B1

(12) **United States Patent**  
Yabunouchi et al.

(10) Patent No.: **US 6,171,994 B1**  
(45) Date of Patent: **Jan. 9, 2001**

(54) **MULTIPLE CROSSLINKING TYPE  
TRANSITION METAL COMPOUND USED  
FOR OLEFIN POLYMERIZATION PROCESS**

(75) Inventors: Nobuhiro Yabunouchi; Kiyohiko Yokota; Masami Watanabe; Takuji Okamoto; Noriyuki Tanii, all of Sodegaura (JP)

(73) Assignee: Idemitsu Kosan Co., Ltd., Tokyo (JP)

(\*) Notice: Under 35 U.S.C. 154(b), the term of this patent shall be extended for 0 days.

(21) Appl. No.: 09/184,279

(22) Filed: Nov. 2, 1998

**Related U.S. Application Data**

(62) Division of application No. 08/619,513, filed on Mar. 29, 1996, now Pat. No. 5,854,165.

(30) **Foreign Application Priority Data**

Sep. 30, 1993 (JP) ..... 5-245129  
Dec. 22, 1993 (JP) ..... 5-324208  
Jul. 8, 1994 (JP) ..... 6-156948

(51) Int. Cl. <sup>7</sup> ..... C08F 4/64

(52) U.S. Cl. ..... 502/117; 556/42; 556/43;  
556/52; 556/53; 556/12; 556/22; 556/23;  
556/11; 502/152; 502/155

(58) Field of Search ..... 556/52, 53, 42,  
556/43, 11, 12, 22, 23; 502/117, 152, 155

(56) **References Cited**

**U.S. PATENT DOCUMENTS**

5,276,208 • 1/1994 Winter et al. ..... 556/53  
5,296,565 • 3/1994 Ueda et al. ..... 526/114  
5,496,902 3/1996 Evertz et al. .....  
5,854,165 12/1998 Yabunouchi et al. .

**FOREIGN PATENT DOCUMENTS**

93/20113 10/1993 (WO) .

**OTHER PUBLICATIONS**

Mengele et al. *Organometallics*, 1993, 12, pp 1931-1935,  
"ansa-metallocene Derivatives, Chiral Zirconocene Complexes with two Dimethylsilylene Bridges", 1993.\*

Hawley et al. *Hawley's Condensed Chemical Dictionary*,  
7th Edition, p. 749, 1987.

Halterman, Ronald L. *Synthesis and Applications of Chiral Cyclopentadienyl Complexes*, pp 965-994, Mar. 1992.

Mengele et al. *Organometallic*, 1993, 12, pp. 1931-1935,  
"ansa-metallocene Derivatives. Chiral Zirconocene Complexes with two Dimethylsilylene Bridges" 1993.

\* cited by examiner

Primary Examiner—David W. Wu

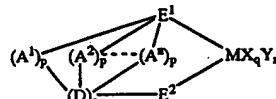
Assistant Examiner—Ling-Siu Choi

(74) Attorney, Agent, or Firm—Oblon, Spivak, McClelland,  
Maier & Neustadt, P.C.

(57) **ABSTRACT**

A novel multiply crosslinked transition metal compound represented by the formula (I):

(I)



wherein M is a metallic element of the Groups 3 to 10 or the lanthanide series of the Periodic Table; E<sup>1</sup> and E<sup>2</sup> are each a σ-bonding or π-bonding ligand; X is a σ-bonding ligand; Y is a Lewis base; A<sup>1</sup>, A<sup>2</sup>, . . . A<sup>n</sup> and D are each a crosslinking group, and at least one of A<sup>1</sup>, A<sup>2</sup>, . . . A<sup>n</sup> comprises a crosslink consisting of carbon alone; n is 2 to 4; p is 1 to 4; q is 1 to 5 and equal to the valence of M minus 2; r is 0 to 3; and s is 0 to 4, and a production process thereof. The transition metal compound is useful as a component of a polymerization catalyst for catalyzing the production of an olefin polymer having a uniform composition and a narrow molecular weight distribution in a high yield.

12 Claims, No Drawings

deteriorates on occasion, and it is more than 1000 m<sup>2</sup>/g, the bulk density of the polymer deteriorates sometimes. Furthermore, in the catalyst of the present invention, the amount of the transition metal in 100 g of the carrier is usually in the range of 0.05 to 10 g, preferably 0.1 to 2 g. If the amount of the transition metal deviates from the above-mentioned range, the activity deteriorates on occasion.

This technique of supporting the components on the carrier enables the formation of the industrially advantageous polymer having the high bulk density and an excellent particle diameter distribution. 10

According to the preparation method of the olefin polymer regarding the present invention, the homopolymerization of an olefin or the copolymerization of an olefin and another olefin and/or another monomer (i.e., the copolymerization of different kinds of olefins, the copolymerization of an olefin and another monomer, or the copolymer of different kinds of olefins and another monomer) can be suitably carried out by the use of the above-mentioned catalyst for polymerization.

~~No particular restriction is put on the kind of olefins, α-olefins having 2 to 20 carbon atoms are preferable. Examples of the α-olefins include ethylene, propylene, 1-butene, 3-methyl-1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, styrene, p-methylstyrene, isopropylstyrene and t-butylstyrene. The above-mentioned other olefin can also suitably be selected.~~

In the present invention, the above-mentioned olefins may be used singly or in a combination of two or more thereof. In the case that two or more olefins are copolymerized, these olefins can optionally be combined. At this time, for example, when propylene is copolymerized with ethylene or ethylene is copolymerized with an α-olefin having 3 to 10 carbon atoms, a copolymerization ratio (molar ratio) of propylene and ethylene, or ethylene and the α-olefin having 3 to 10 carbon atoms is usually selected in the range of 99.9:0.1 to 0.1 to 99.9, preferably 99.5:0.5 to 75.0:25.0. 30

In the present invention, the above-mentioned olefin may be copolymerized with another monomer, and examples of the other monomer which can be used at this time include chain diolefins such as butadiene, isoprene and 1,5-hexadiene, cyclic olefins such as norbornene, 1,4,5,8-dimethanol-1,2,3,4,4a,5,8,8a-octahydronaphthalene and 2-norbornene, cyclic diolefins such as norbornadiene, 5-ethylidene norbornene, 5-vinyl norbornene and dicyclopentadiene, unsaturated esters such as ethyl acrylate and methyl methacrylate, lactones such as β-propiolactone, β-butyrolactone and γ-butyrolactone, lactams such as ε-caprolactam and δ-valerolactam, and epoxides such as epoxypropane and 1,2-epoxybutane. 45

Incidentally, the catalyst for polymerization of the present invention can be used not only for the polymerization of the above-mentioned olefin but also for the polymerization of a monomer other than the olefin. 50

In the present invention, no particular restriction is put on a polymerization method, and any of a slurry polymerization method, a gaseous phase polymerization method, a bulk polymerization method, a solution polymerization method and a suspension polymerization method can be used, but the slurry polymerization method and the gaseous phase polymerization method are preferable from the viewpoints of a high productivity and less process steps. 55

With regard to the conditions of the polymerization, a polymerization temperature is usually in the range of -100 to 250° C., preferably -50 to 200° C., more preferably 0 to

130° C. Furthermore, a use ratio of the catalyst to the reaction material is such that the material monomer/the above-mentioned component (A) (molar ratio) is preferably in the range of 1 to 10<sup>8</sup>, more preferably 100 to 10<sup>3</sup>. Moreover, a polymerization time is usually in the range of 5 minutes to 10 hours, and a reaction pressure is preferably in the range of from atmospheric pressure to 200 kg/cm<sup>2</sup>G, more preferably from atmospheric pressure to 100 kg/cm<sup>2</sup>G.

The molecular weight of the polymer can be adjusted by selecting the kinds and the amounts of catalytic components and the polymerization temperature, and by carrying out the polymerization in the presence or absence of hydrogen.

In the case that a polymerization solvent is employed, examples of the usable solvent include aromatic hydrocarbons such as benzene, toluene, xylene and ethylbenzene, alicyclic hydrocarbons such as cyclopentane, cyclohexane and methylcyclohexane, aliphatic hydrocarbons such as pentane, hexane, heptane and octane, and halogenated hydrocarbons such as chloroform and dichloromethane. These solvents may be used singly or in a combination of two or more thereof. In addition, a monomer such as an α-olefin may be used as the solvent. In a certain polymerization method, the polymerization can be carried out in the absence of any solvent.

No particular restriction is put on the molecular weight of the polymer which can be obtained by such a process, but its intrinsic viscosity  $[\eta]$  (measured in decalin at 135° C.) is preferably 0.1 dl/g or more, more preferably 0.2 dl/g or more. If the intrinsic viscosity is less than 0.1 dl/g, sufficient mechanical properties cannot be obtained, and hence the polymer having such a low intrinsic viscosity is not practical.

In the present invention, prepolymerization can be carried out by the use of the above-mentioned catalyst for polymerization. The prepolymerization can be accomplished by bringing a small amount of an olefin into contact with the solid catalytic component, but its procedure is not particularly limited and a known method can be used. No particular restriction is put on the olefin for use in the prepolymerization, and such olefins as mentioned above, for example, ethylene, α-olefins having 3 to 20 carbon atoms and mixtures thereof are usable, but it is advantageous to employ the same olefin as used in the polymerization. 30

A prepolymerization temperature is usually in the range of -20 to 200° C., preferably -10 to 130° C., more preferably 0 to 80° C. In the prepolymerization, an inactive hydrocarbon, an aliphatic hydrocarbon, an aromatic hydrocarbon or a monomer can be used as the solvent. Above all, the aliphatic hydrocarbon is particularly preferable. The prepolymerization may be carried out in the absence of any solvent.

In the prepolymerization, conditions are desirably regulated so that the intrinsic viscosity  $[\eta]$  (~~at 135° C.~~) of a prepolymerized product may be 0.2 dl/g or more, preferably 0.5 dl/g or more and so that the amount of the prepolymerized product per mmol of the transition metal component in the catalyst may be in the range of 1 to 10,000 g, preferably 10 to 1,000 g.

Thus, an olefin polymer of the present invention having a uniform composition and a narrow molecular weight distribution can efficiently be obtained. 55

Next, the present invention will be described in more detail with reference to examples, but the scope of the present invention should not be limited at all by these examples. 60

#### REFERENCE PREPARATION EXAMPLE 1

Preparation of (1,1'-dimethylsilylene)(2,2'-dimethylsilylene)-bis(cyclopentadienyl)zirconium dichloride (A-2)

2.4 g (9.6 mmol) of (1,1'-dimethylsilylene)(2,2'-dimethylsilylene)-bis(cyclopentadiene) was dissolved in 50

TEST AVAILABLE COPY

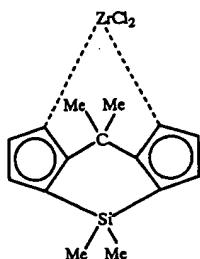
ence Preparation Example 1. The results are shown in Table 1.

TABLE 1-1

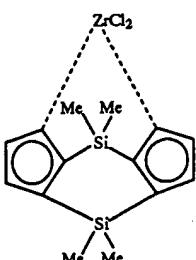
	Catalyst		Polymer		5
	Main Catalyst	Cocatalyst	Kind	Yield (g)	
Example 2	A-1	TIBA B-1	Ethylene-1-octene Copolymer	45.7	10
Example 3	A-1	MAO	Ethylene-1-octene Copolymer	35.1	
Example 4	A-1	TIBA B-1	Polyethylene	37.4	
Example 5	A-1	MAO	Polyethylene	30.9	15
Ref. Ex. 1	A-2	TIBA B-1	Ethylene-1-octene Copolymer	29.5	
Ref. Ex. 2	A-2	MAO	Ethylene-1-octene Copolymer	27.3	
Ref. Ex. 3	A-2	TIBA B-1	Polyethylene	35.0	
Ref. Ex. 4	A-2	MAO	Polyethylene	25.6	20

## Notes

A-1: (1,1'-dimethylsilylene)-(2,2'-isopropylidene)-bis(cyclopentadienyl)zirconium dichloride



A-2: (1,1'-dimethylsilylene)-(2,2'-dimethylsilylene)-bis(cyclopentadienyl)zirconium dichloride



TIBA: Triisobutylaluminum

B-1: N,N'-dimethylanilinium tetrakis (pentafluorophenyl) borate

MAO: Methylaluminoxane

TABLE 1-2

	Polymer			
	Intrinsic* Viscosity [η] (dL/g)	Melting Point** (°C)	1-octene Unit Content (mol %)	Melting Energy** ΔH (J/g)
Example 2	0.92	108.7	5.8	22
Example 3	0.49	109.8	7.3	13
Example 4	2.37	133.5	—	200
Example 5	1.87	135.8	—	257
Ref. Ex. 1	0.80	115.6	4.0	92
Ref. Ex. 2	0.87	115.5	3.9	58
Ref. Ex. 3	2.82	135.0	—	200
Ref. Ex. 4	3.51	133.5	—	200

\*The intrinsic viscosity was determined at 30°C.

\*\*The melting point was determined on the basis of the results of second heat at a heating rate of 10° C/min by the use of DSC.

As understood from Table 1, in the case that (1,1'-dimethylsilylene)-(2,2'-isopropylidene)-bis(cyclopentadienyl)zirconium dichloride is used as a main catalytic component, the copolymerizability of ethylene-1-octene copolymerization is better than in the case that (1,1'-dimethylsilylene)-(2,2'-dimethylsilylene)-bis(cyclopentadienyl)zirconium dichloride is used.

## EXAMPLE 6

Preparation of (1,1'-dimethylsilylene)-(2,2'-isopropylidene)-bis(cyclopentadienyl)titanium dichloride (A-3)

2.3 g (10 mmol) of (1,1'-dimethylsilylene)-(2,2'-isopropylidene)-bis(cyclopentadiene) was dissolved in 100 ml of hexane, and 20 mmol of n-butyllithium was added dropwise at -78° C. to the solution, followed by stirring at room temperature for 12 hours. Next, the solvent was distilled off, and the resultant residue was washed with 50 ml of hexane, and then dried under reduced pressure to obtain a white solid. Afterward, this solid was suspended in 50 ml of tetrahydrofuran, and a tetrahydrofuran solution containing 3.7 g (10 mmol) of a titanium trichloride-three tetrahydrofuran complex was added at -78° C. to the suspension. Next, the temperature of the solution was gradually returned to room temperature, followed by stirring for 12 hours. Afterward, 4.3 g (30 mmol) of silver chloride was added to this suspension, and the mixture was then stirred at room temperature for 2 days. The solvent was distilled off, and recrystallization was then carried out from ether to obtain 0.2 g of (1,1'-dimethylsilylene)-(2,2'-isopropylidene)-bis(cyclopentadienyl)titanium dichloride in the state of a red powder.

The <sup>1</sup>H-NMR of this product was measured, and the following results were obtained.

1H-NMR (90 MHz, CDCl<sub>3</sub>): δ0.43 [3H, s, (CH<sub>3</sub>)<sub>2</sub>Si], 1.02 [3H, s, (CH<sub>3</sub>)<sub>2</sub>Si], 1.36 (3H, s, (CH<sub>3</sub>)<sub>2</sub>C), 2.18 (3H, s, (CH<sub>3</sub>)<sub>2</sub>C), 6.3-7.1 (6H, m, —CH—).

In addition, some peaks attributed to impurities were slightly observed.

## EXAMPLE 7

In a 1-liter autoclave heated and dried under reduced pressure were placed 360 ml of toluene, 40 ml of 1-octene and 1 mmol of triisobutylaluminum (TIBA) at room temperature under a nitrogen atmosphere, and the temperature of the solution was then raised up to 60° C. with stirring.

Afterward, 1  $\mu\text{mol}$  of (1,1'-dimethylsilylene)(2,2'-isopropylidene)-bis(cyclopentadienyl)titanium dichloride obtained in Example 6 and 1  $\mu\text{mol}$  of N,N'-dimethylanilinium tetrakis(pentafluorophenyl)borate were placed in the autoclave at 60° C., and the mixture was then heated up to 80° C. Next, while ethylene was continuously introduced into the autoclave at 80° C. so as to maintain 8 atm, polymerization was carried out for 1 hour.

After the completion of the reaction, the resultant reaction product was poured into a methanol-hydrochloric acid solution, and then sufficiently stirred, followed by filtration. Next, the collected product was sufficiently washed with methanol, and then dried to obtain a polymer. The results are shown in Table 2.

## EXAMPLE 8

The same procedure as in Example 7 was repeated except that 1 mmol of TIBA was replaced with 6 mmol of methylaluminoxane and N,N'-dimethylanilinium tetrakis(pentafluorophenyl)borate was not used. The results are shown in Table 2.

## EXAMPLE 9

The same procedure as in Example 7 was repeated except that 40 ml of 1-octene was not used. The results are shown in Table 2.

## EXAMPLE 10

The same procedure as in Example 8 was repeated except that 40 ml of 1-octene was not used. The results are shown in Table 2.

TABLE 2-1

	Catalyst		Kind	Yield (g)
	Main Catalyst	Cocatalyst		
Example 7	A-3	TIBA B-1	Ethylene-1-octene Copolymer	0.85
Example 8	A-3	MAO	Ethylene-1-octene Copolymer	1.90
Example 9	A-3	TIBA B-1	Polyethylene	12.7
Example 10	A-3	MAO	Polyethylene	8.90

A-3: (1,1'-dimethylsilylene)(2,2'-isopropylidene)-bis(cyclopentadienyl)titanium dichloride

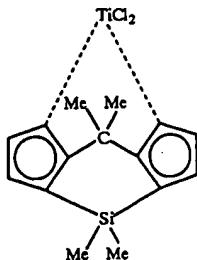


TABLE 2-2

	Polymer				
	Intrinsic* Viscosity [η] (dl/g)	Melting Point** (°C)	1-octene Unit Content (mol %)	Catalytic Activity (kg/g Ti/hr)	Melting Energy** ΔH (J/g)
Example 7	2.00	None	10.4	18	10.0
Example 8	2.96	None	9.8	40	11.3
Example 9	7.38	135	—	265	144
Example 10	—	134	—	186	126

\*The intrinsic viscosity was determined at 125° C.

\*\*The melting point was determined on the basis of the results of second heat at a heating rate of 10° C./min by the use of DSC.

## EXAMPLE 11

## Preparation of (1,1'-dimethylsilylene)-(2,2'-isopropylidene)-bis(cyclopentadienyl)titanium dichloride (A-4)

5.57 g (24.2 mmol) of (1,1'-dimethylsilylene)(2,2'-isopropylidene)-bis(cyclopentadiene) was dissolved in 100 ml of THF (tetrahydrofuran), and 48.8 mmol of n-butyllithium was added dropwise at -78° C. to the solution, followed by stirring at room temperature for 8 hours. Next, the solvent was distilled off, and the resultant residue was washed with 100 ml of hexane and next 100 ml of THF, and then dried under reduced pressure to obtain 1.00 g (4.16 mmol) of a white solid of a lithium salt. Afterward, this solid was suspended in 50 ml of tetrahydrofuran, and a tetrahydrofuran solution (60 ml) containing 1.54 g (4.16 mmol) of a titanium trichloride-three tetrahydrofuran complex was added at room temperature to the suspension, followed by stirring for 12 hours. Next, 11.08 g (77 mmol) of silver chloride was added to this suspension, and the mixture was then stirred at room temperature for 3 hours. The solvent was distilled off, and extraction with ether, the removal of ether by distillation and washing with hexane were done in turn to obtain 35 mg of (1,1'-dimethylsilylene)(2,2'-isopropylidene)-bis(cyclopentadienyl)-titanium dichloride in the state of a red powder.

The  $^1\text{H-NMR}$  of this product was measured, and the following results were obtained.

$^1\text{H-NMR}$  (90 MHz,  $\text{CDCl}_3$ ): 80.43 [3H, s,  $(\text{CH}_3)_2\text{Si}$ ], 1.02 [3H, s,  $(\text{CH}_3)_2\text{Si}$ ], 1.36 (3H, s,  $(\text{CH}_3)_2\text{C}$ ), 2.18 (3H, s,  $(\text{CH}_3)_2\text{C}$ ), 6.3-7.1 (6H, m,  $-\text{CH}-$ ).

## EXAMPLE 12

In a 1-liter autoclave heated and dried under reduced pressure were placed 360 ml of toluene, 40 ml of 1-octene and 1 mol of triisobutylaluminum (TIBA) at room temperature under a nitrogen atmosphere, and the temperature of the solution was then raised up to 60° C. with stirring.

Afterward, 1  $\mu\text{mol}$  of (1,1'-dimethylsilylene)(2,2'-isopropylidene)-bis(cyclopentadienyl)titanium dichloride obtained in Example 11 and 1  $\mu\text{mol}$  of N,N'-dimethylanilinium tetrakis(pentafluorophenyl)borate were placed in the autoclave at 60° C., and the mixture was then heated up to 80° C. Next, while ethylene was continuously introduced into the autoclave at 80° C. so as to maintain 8 atm, polymerization was carried out for 1 hour.

After the completion of the reaction, the resultant reaction product was poured into a methanol-hydrochloric acid solution, and then sufficiently stirred, followed by filtration. Next, the collected product was sufficiently washed with methanol, and then dried to obtain a polymer.



US005478890A

United States Patent [19]  
Shinozaki et al.

[11] Patent Number: 5,478,890  
[45] Date of Patent: \* Dec. 26, 1995

BEST AVAILABLE COPY

## [54] OLEFIN POLYMER COMPOSITION

[75] Inventors: Tetsunori Shinozaki; Mamoru Kioka, both of Yamaguchi, Japan

[73] Assignee: Mitsui Petrochemical Industries, Ltd., Tokyo, Japan

[\*] Notice: The portion of the term of this patent subsequent to Aug. 1, 2012, has been disclaimed.

[21] Appl. No.: 193,859

[22] Filed: Feb. 9, 1994

## Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 81,706, Jun. 25, 1993, abandoned, which is a continuation-in-part of Ser. No. 929,518, Aug. 14, 1992, abandoned.

## [30] Foreign Application Priority Data

Aug. 14, 1991	[JP]	Japan	3-204464
Aug. 14, 1991	[JP]	Japan	3-204465
Aug. 14, 1991	[JP]	Japan	3-204466
Aug. 14, 1991	[JP]	Japan	3-204467

[51] Int. Cl. 6 C08L 47/00

[52] U.S. Cl. 525/240; 525/232; 525/86; 525/288; 525/289; 525/290; 525/297; 525/268

[58] Field of Search 525/232, 240, 525/86

## [56] References Cited

## U.S. PATENT DOCUMENTS

3,963,801	6/1976	Su	525/166
5,015,694	5/1991	Milani et al.	.
5,021,382	6/1991	Malpass, Jr. et al.	.
5,041,491	8/1991	Turke.	.
5,262,228	11/1993	Kohyama et al.	.
5,438,100	8/1995	Shinozaki et al.	525/240

## FOREIGN PATENT DOCUMENTS

0354893	2/1990	European Pat. Off.	.
0401993	12/1990	European Pat. Off.	.
0424145	4/1991	European Pat. Off.	.

Primary Examiner—Vasu S. Jagannathan

Attorney, Agent, or Firm—Sherman and Shalloway

## [57] ABSTRACT

The olefin polymer composition according to the invention comprises [I] an  $\alpha$ -olefin/polyene copolymer-containing polymer in an amount of 0.005 to 99 by weight, said  $\alpha$ -olefin/polyene copolymer-containing polymer comprising (i) an  $\alpha$ -olefin/polyene copolymer and (ii) a polyethylene, and [II] a polyethylene in an amount of 1 to 99.995 % by weight. The olefin polymer composition comprising the  $\alpha$ -olefin/polyene copolymer-containing polymer [I] and the olefin polymer [II] has a high melt tension and an excellent moldability in an inflation molding, and further it can be molded into a large sized container, etc. by means of a blow molding or the like.

16 Claims, 1 Drawing Sheet

1

## OLEFIN POLYMER COMPOSITION

## CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 08/081,706, filed Jun. 25, 1993, now abandoned; which, in turn, is a continuation-in-part of co-pending application Ser. No. 07/929,518, filed Aug. 14, 1992, now abandoned.

## FIELD OF THE INVENTION

The present invention relates to an olefin polymer composition, and more particularly to an olefin polymer composition comprising an  $\alpha$ -olefin/polyene copolymer-containing polymer and having a high melt tension.

## BACKGROUND OF THE INVENTION

Olefin polymers such as high-density polyethylene, linear low-density polyethylene, polypropylene are excellent in not only transparency but also mechanical strength such as rigidity and impact strength, and have been conventionally molded into films by means of inflation molding, injection molding, extrusion molding, etc.

Such olefin polymers as mentioned above generally are low in the melt tension (MT), so that they are difficultly molded into large capacity containers (e.g., bottles) for example by a blow molding or difficultly molded into liners of electrical appliances for example by a vacuum molding. By those restrictions in the molding processes, the resulting molded products are also restricted. That is, the use applications of the olefin polymers are restricted in spite that they have various excellent properties.

Further, as for polypropylene, there are such problems that a phenomenon of drawdown occurs and molding conditions are restricted when propylene is molded into a film by an inflation molding, because of its low melt tension. For coping with those problems, a method of adding a high-pressure low-density polyethylene or the like to polypropylene is carried out in the conventional inflation molding process to increase the melt tension thereby to stabilize bubbles. However, this method sometimes induces decrease of the film strength and decrease of a film transparency.

Accordingly, if olefin polymers (e.g., polypropylene) having a high melt tension are developed, it becomes possible to form large capacity containers such as bottles by a blow molding and to form liners of electrical appliances by a vacuum molding from those polymers, and hence the use applications of the olefin polymers can be much more extended.

Further, when the olefin polymers having a high melt tension are molded into films by means of an inflation molding, the bubbles can be stabilized and the molding speed can be made higher.

For these reasons, an advent of olefin polymers such as polypropylene, high-density polyethylene and linear low-density polyethylene having high melt tension has been eagerly desired.

The present inventors have studied on the olefin polymers of high melt tension to comply with the above-mentioned requirements, and as a result, they have found that an  $\alpha$ -olefin/polyene copolymer-containing polymer of high melt tension can be obtained by a process of copolymerizing an  $\alpha$ -olefin and a polyene to a catalyst for olefin polymerization which comprises a transition metal compound cata-

2

lyst component and an organometallic compound catalyst component, and then polymerizing olefin to the resulting product. The present inventors have further studied earnestly based on this finding, and they have found that an olefin polymer composition comprising an  $\alpha$ -olefin/polyene copolymer-containing polymer and a conventionally known olefin polymer, said  $\alpha$ -olefin/polyene copolymer-containing polymer being obtained by copolymerizing an  $\alpha$ -olefin and a polyene in the presence of a catalyst for olefin polymerization and then polymerizing olefin to the resulting product as mentioned above, shows a high melt tension and a high moldability in the molding procedure such as an inflation molding, and can be molded even by an inflation molding, etc. Thus, the present invention has been accomplished.

## OBJECT OF THE INVENTION

The object of the present invention is to provide an olefin polymer composition which shows a high moldability when it is molded into for example a film and has a high melt tension so that it can be molded into a large capacity container by mean of a blow molding, although such molding is hardly applicable conventionally.

## SUMMARY OF THE INVENTION

There is provided by the present invention an olefin polymer composition comprising:

[I] an  $\alpha$ -olefin/polyene copolymer-containing polymer in an amount of 0.005 to 99% by weight, said  $\alpha$ -olefin/polyene copolymer-containing polymer comprising:

(i) an  $\alpha$ -olefin/polyene copolymer, and

(ii) an olefin polymer; and

[II] an olefin polymer in an amount of 1 to 99.995% by weight

wherein the polyene has 7 or more carbon atoms and having an olefinic double bond at both terminals, and the  $\alpha$ -olefin/polyene copolymer contains constituent units derived from the  $\alpha$ -olefin in an amount of 99.99% to 70 mol % and contains constituent units derived from the polyene in an amount of 0.001 to 30 mol %,

the olefin polymer (ii) is a polymer of ethylene,

the  $\alpha$ -olefin/polyene copolymer-containing polymer [I] contains the  $\alpha$ -olefin/polyene copolymer (i) in an amount of 0.001 to 99% by weight and contains the olefin polymer (ii) in an amount of 99.99% to 1% by weight, and

the olefin polymer [II] is a polymer of ethylene.

The  $\alpha$ -olefin/polyene copolymer-containing polymer [I] can be prepared by polymerizing or copolymerizing olefin to a prepolymerized catalyst so as to form the olefin polymer (ii), said prepolymerized catalyst comprising the  $\alpha$ -olefin/polyene copolymer (i) obtained by copolymerizing an  $\alpha$ -olefin and a polyene to a catalyst component which comprises:

[A] a transition metal compound catalyst component, and

[B] an organometallic compound catalyst component containing a metal selected from metals in Group I to Group III of the periodic table,

in the total amounts of the  $\alpha$ -olefin and the polyene compound of 0.01 to 2,000 g per 1 g of the transition metal compound catalyst component [A].

Such olefin polymer composition comprising the  $\alpha$ -olefin/polyene copolymer-containing polymer [I] and the olefin polymer [II] as mentioned above has a high melt tension and a high moldability in the inflation molding procedure and

can be molded into a large capacity container or the like by means of a blow molding, etc.

#### BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a view illustrating steps of a process for preparing an  $\alpha$ -olefin/polyene copolymer-containing polymer [I] used in the invention.

#### DETAILED DESCRIPTION OF THE INVENTION

The olefin polymer composition according to the present invention is described in detail hereinafter.

The term "polymerization" used in the invention sometimes means not only "homopolymerization" but also "copolymerization", and the term "polymer" used in the invention sometimes means not only "homopolymer" but also "copolymer".

The olefin polymer composition according to the invention comprises:

[I] an  $\alpha$ -olefin/polyene copolymer-containing polymer, and

[II] an olefin polymer.

In FIG. 1, the steps of a process for preparing the  $\alpha$ -olefin/polyene copolymer-containing polymer [I] used in the invention are illustrated.

At first, the  $\alpha$ -olefin/polyene copolymer-containing polymer [I] used in the invention is described.

The  $\alpha$ -olefin/polyene copolymer-containing polymer [I] used in the invention comprises:

(i) an  $\alpha$ -olefin/polyene copolymer, and

(ii) an olefin polymer.

Such  $\alpha$ -olefin/polyene copolymer-containing polymer [I] can be obtained by, for example, polymerizing or copolymerizing olefin to a prepolymerized catalyst so as to form an olefin polymer (ii), said prepolymerized catalyst comprising the  $\alpha$ -olefin/polyene copolymer (i) which is obtained by copolymerizing an  $\alpha$ -olefin and a polyene compound to a catalyst component comprising [A] a transition metal compound catalyst component and [B] an organometallic compound catalyst component.

The  $\alpha$ -olefin and the polyene compound used for preparing the  $\alpha$ -olefin/polyene copolymer (ii) will be described below.

The  $\alpha$ -olefins employable in the invention are  $\alpha$ -olefins of 2-20 carbon atoms. Concrete examples of such  $\alpha$ -olefins include ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 3-methyl-1-butene, 1-methyl-1-pentene, 4-methyl-1-pentene, 1-hexene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, and 1-eicosene. They can be used singly or in combination.

The  $\alpha$ -olefin used herein may be the same or different from an  $\alpha$ -olefin which is used for preparing the olefin polymer (ii) described later.

Among the above-exemplified  $\alpha$ -olefins, preferably used are ethylene, propylene, 1-butene, 4-methyl-1-pentene, 3-methyl-1-butene and 1-eicosene.

Concrete examples of the polyene compounds include:

aliphatic polyene compounds such as 4-methyl-1,4-hexadiene, 5-methyl-1,4-hexadiene, 6-methyl-1,6-octadiene, 7-methyl-1,6-octadiene, 6-ethyl-1,6-octadiene, 6-propyl-1,6-octadiene, 6-butyl-1,6-octadiene, 6-methyl-1,6-nonadiene, 7-methyl-1,6-nonadiene, 6-ethyl-1,6-nonadiene, 7-ethyl-1,6-nonadiene, 6-methyl-1,6-decadiene, 7-methyl-1,6-decadiene, 6-methyl-1,6-

undecadiene, 1,4-hexadiene, 1,5-hexadiene, 1,6-heptadiene, 1,6-octadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,13-tetradecadiene, 1,5,9-decatriene butadiene and isoprene;

vinylcyclohexene, vinylnorbornene, ethylidene-norbornene, dicyclopentadiene, cyclooctadiene, 2,5-norbornadiene;

acyclic polyene compounds such as 1,4-divinylcyclohexane, 1,3-divinylcyclohexane, 1,3-divinylcyclopentane, 1,5-divinylcyclooctane, 1-allyl-4-vinylcyclohexane, 1,4-diallylcyclohexane, 1-allyl-5-vinylcyclooctane, 1,5-diallylcyclooctane, 1-allyl-4-isopropenylcyclohexane, 1-isopropenyl-4-vinylcyclohexane and 1-isopropenyl-3-vinylcyclopentane; and

aromatic polyene compounds such as divinylbenzene and vinylisopropenylbenzene.

They are used singly or in combination.

Among the above-mentioned polyene compounds, preferably used in the invention are polyene compounds having 7 or more carbon atoms and having an olefinic double bond at the both terminals, and more preferably used are aliphatic or alicyclic polyene compounds having an olefinic double bond at the both terminals.

Concrete examples of such preferable polyene compounds include 1,6-heptadiene, 1,7-octadiene, 1,9-decadiene, 1,13-tetradecadiene, 1,5,9-decatriene, 1,4-divinylcyclohexane, 1,3-divinylcyclopentane, 1,5-divinylcyclooctane, 1-allyl-4-vinylcyclohexane, 1,4-diallylcyclohexane and 1,3,4-trivinylcyclohexane.

Of these, preferred are aliphatic polyene compounds having 8 or more carbon atoms, preferably 10 or more carbon atoms, and particularly preferred are straight-chain aliphatic polyene compounds having 10 or more carbon atoms.

In the present invention, the  $\alpha$ -olefin/polyene copolymer (i) is preferably a high-molecular-weight copolymer. The melt flow rate of the  $\alpha$ -olefin/polyene copolymer (i) is preferably 0.1 dg/min. or less, more preferably 0.01 dg/min. or less.

In the preparation of the  $\alpha$ -olefin/polyene copolymer (i), the  $\alpha$ -olefin and the polyene compound are preferably copolymerized in the following combinations:

ethylene/1,7-octadiene, ethylene/1,9-decadiene, ethylene/1,13-tetradecadiene, ethylene/1,5,9-decatriene,

propylene/1,7-octadiene, propylene/1,9-decadiene, propylene/1,13-tetradecadiene, propylene/1,5,9-decatriene, butene/1,9-decadiene, butene/1,5,9-decatriene, 4-methyl-1-pentene/1,9-decadiene, 3-methyl-1-butene/1,9-decadiene, 1-eicosene/1,9-decadiene, propylene/1,4-divinylcyclohexane, and butene/1,4-divinylcyclohexane.

The  $\alpha$ -olefin/polyene copolymer (i) is desired to contain constituent units derived from the  $\alpha$ -olefin in an amount of generally 99.99% to 50% by mol, preferably 99.99% to 70% by mol, more preferably 99.95% to 75% by mol, much more preferably 99.9% to 80% by mol, most preferably 99.95% to 85% by mol, and to contain constituent units derived from the polyene compound in an amount of generally 0.001 to 50% by mol, preferably 0.001 to 30% by mol, more preferably 0.005 to 25% by mol, much more preferably 0.01 to 20% by mol, most preferably 0.05 to 15% by mol.

Further, the  $\alpha$ -olefin/polyene copolymer (i) may also contain constituent units derived from other olefins described later in such an amount that the objects of the invention are not marred. In this case, the constituent units derived from other olefins are contained in the  $\alpha$ -olefin/

TEST AVAILABLE COPY

polyene copolymer (i) in an amount of generally less than 30% by mol, preferably not more than 20% by mol, more preferably not more than 15% by mol.

The composition ratio in the above-mentioned  $\alpha$ -olefin/polyene copolymer can be determined by measuring the amounts of the  $\alpha$ -olefin and the polyene compound consumed in the prepolymerization reaction. Concretely, the constituent units [P] (% by mol) can be calculated as follows.

$$[P] (\% \text{ by mol}) = \frac{([P_0] - [P_r]) \times 100}{([P_0] - [P_r]) + ([\alpha_0] - [\alpha_r])}$$

In the above formula, each symbols have the following meanings.

[ $P_0$ ]: number of moles of the polyene compound fed in the prepolymerization

[ $P_r$ ]: number of moles of the unreacted polyene compound

[ $\alpha_0$ ]: number of moles of the  $\alpha$ -olefin fed in the prepolymerization

[ $\alpha_r$ ]: number of the unreacted  $\alpha$ -olefin

[ $\alpha_r$ ] and [ $P_r$ ] in the above formula can be determined by measuring the unreacted  $\alpha$ -olefin and the unreacted polyene compound both remaining in the polymerizer by means of gas chromatography, etc.

Examples of the olefins used for preparing the olefin polymer (ii) for forming the  $\alpha$ -olefin/polyene copolymer-containing polymer [I] are the aforementioned  $\alpha$ -olefins of 2 to 20 carbon atoms, preferably ethylene.

Also employable are:

aromatic vinyl compounds such as styrene, substituted styrenes (e.g., dimethyl styrene), allylbenzene, substituted allylbenzenes (e.g., allyltoluene), vinylnaphthalene, substituted vinylnaphthalenes, allylnaphthalene and substituted allylnaphthalenes;

alicyclic vinyl compounds such as vinylcyclohexane, substituted vinylcyclohexanes, vinylcyclopentane, substituted vinylcyclopentanes, vinylcycloheptane, substituted vinylcycloheptanes and allylnorbornane;

cyclic olefins such as cyclopentene, cycloheptene, norbornene, 5-methyl-2-norbornene, tetracyclododecene and 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8a-ocahydronaphthalene;

silane type unsaturated compounds such as allyltrimethylsilane, allyltriethylsilane, 4-trimethylsilyl-1-butene, 6-trimethylsilyl-1-hexene, 8-trimethylsilyl-1-octene and 10-trimethylsilyl-1-decene; and

the aforementioned polyene compounds.

They can be employed singly or in combination.

Of these, preferably used is ethylene.

The  $\alpha$ -olefin/polyene copolymer-containing polymer [I] contains the  $\alpha$ -olefin/polymer copolymer (i) in an amount of 0.001 to 99% by weight, preferably 0.005 to 90% by weight, more preferably 0.01 to 88% by weight, and contains the olefin polymer (ii) in an amount of 99.999 to 1% by weight, preferably 99.995 to 10% by weight, more preferably 99.99 to 12% by weight.

Among such olefin polymers according to the invention, particularly preferred is an olefin polymer containing the  $\alpha$ -olefin/polyene copolymer (i) in an amount of 0.001 to 15% by weight, especially 0.008 to 10% by weight and the olefin polymer (ii) in an amount of 99.999 to 85% by weight, especially 99.992 to 90% by weight.

The melt flow rate (MFR) of the olefin polymer according to the invention, as measured in accordance with ASTM D1238 (polyethylene: 190° C., 2.16 kg), is not more than

5000 g/10 min., preferably in the range of 0.01 to 3000 g/10 min., more preferably 0.02 to 2000 g/10 min., most preferably 0.05 to 1000 g/10 min.

Such  $\alpha$ -olefin/polyene copolymer-containing polymer [I] has a high melt tension (MT).

In the  $\alpha$ -olefin/polyene copolymer-containing polymer [I] used in the invention, the melt tension (MT) and the melt flow rate (MFR) satisfy the following relation.

For example, if the  $\alpha$ -olefin/polyene copolymer (i) and the olefin polymer (ii) both constituting the  $\alpha$ -olefin/polyene copolymer-containing polymer [I] are an ethylene/polyene copolymer and propylene homopolymer, respectively, the melt Lens ion and the melt flow rate in this  $\alpha$ -olefin/polyene copolymer-containing polymer [I] satisfy the following relation:

generally,  $\log[MT] \geq -0.8\log[MFR] + 0.3$ ;

preferably,  $\log[MT] \geq -0.8\log[MFR] + 0.5$ ;

more preferably,  $\log[MT] \geq -0.8\log[MFR] + 0.7$ ;

most preferably,  $\log[MT] \geq -0.8\log[MFR] + 0.8$ .

Further when the olefin polymer (ii) is propylene random polymer the melt tension and the melt flow rate in this  $\alpha$ -olefin/polyene copolymer-containing polymer [I] satisfy the above-mentioned relation.

If the  $\alpha$ -olefin/polyene copolymer (i) is a copolymer of  $\alpha$ -olefin having 3 or more carbon atoms and polyene and the olefin polymer (ii) is polypropylene in the  $\alpha$ -olefin/polyene copolymer-containing polymer [I], the melt tension and the melt flow rate in this  $\alpha$ -olefin/polyene copolymer-containing polymer [I] satisfy the following relation:

generally,  $\log[MT] \geq -0.8\log[MFR] + 0.30$ ;

preferably,  $\log[MT] \geq -0.8\log[MFR] + 0.35$ ;

more preferably,  $\log[MT] \geq -0.8\log[MFR] + 0.40$ .

By the way when a melt tension of the olefin polymer (ii) is represented as  $[MT_0]$ , a melt tension of the  $\alpha$ -olefin/polyene copolymer-containing polymer is represented as [MT] and a weight percentage of the  $\alpha$ -olefin/polyene copolymer (i) in the  $\alpha$ -olefin/polyene copolymer-containing polymer is represented as [C], these  $[MT_0]$ , [MT] and [C] satisfy the following relation:

$$\frac{[MT]}{[MT_0]} \geq \frac{1}{20} \log[C] + 1.25$$

preferably

$$\frac{[MT]}{[MT_0]} \geq \frac{1}{10} \log[C] + 1.50$$

more preferably

$$\frac{[MT]}{[MT_0]} \geq \frac{3}{20} \log[C] + 1.75$$

most preferably

$$\frac{[MT]}{[MT_0]} \geq \frac{1}{5} \log[C] + 2.00$$

Furthermore, when the  $\alpha$ -olefin/polyene copolymer-containing polymer [I] is composed of the ethylene/polyene copolymer (i) and polyethylene (ii) as described above and has a density of about 0.92 g/cm<sup>3</sup> and MFR of 1 g/10 min., the melt tension of this  $\alpha$ -olefin/polyene copolymer-containing polymer is not less than 2.5 g, preferably not less than 3.5 g, more preferably not less than 4.0 g, much more preferably not less than 4.5 g, most preferably not less than 5.0 g.

An intrinsic viscosity  $[\eta]$  of the olefin polymer, according to the invention, measured in decalin at  $135^{\circ}\text{C}$ , is in the range of 0.05 to 20 dl/g, preferably 0.1 to 15 dl/g, more preferably 0.2 to 13 dl/g.

In the olefin polymer of the invention, the melt tension (MT) and an intrinsic viscosity  $[\eta]$  also satisfy the following relation.

For example, if the  $\alpha$ -olefin/polyene copolymer (i) and the olefin polymer (ii) both constituting the olefin polymer of the invention are an ethylene/polyene copolymer and polypropylene, respectively, the melt tension and the intrinsic viscosity  $[\eta]$  in this olefin polymer satisfy the following relation:

generally,  $\log[\text{MT}] \geq 3.7 \log ([\eta]) - 1.5$ ;

preferably,  $\log[\text{MT}] \geq 3.7 \log ([\eta]) - 1.3$ ;

more preferably,  $\log[\text{MT}] \geq 3.7 \log ([\eta]) - 1.1$ ;

most preferably,  $\log[\text{MT}] \geq 3.7 \log ([\eta]) - 1.0$ .

If the  $\alpha$ -olefin/polyene copolymer (i) is a copolymer of  $\alpha$ -olefin of 3 or more carbon atoms and polyene and the olefin polymer (ii) is polypropylene in the olefin polymer of the invention, the melt tension and the intrinsic viscosity in this olefin polymer satisfy the following relation:

generally,  $\log[\text{MT}] \geq 3.7 \log ([\eta]) - 1.50$ ;

preferably,  $\log[\text{MT}] \geq 3.7 \log ([\eta]) - 1.45$ ;

more preferably,  $\log[\text{MT}] \geq 3.7 \log ([\eta]) - 1.40$ .

Furthermore, when the olefin polymer of the invention is composed of an ethylene/polyene copolymer (i) and polyethylene (ii) as described above and has a density of about  $0.92 \text{ g/cm}^3$  and the intrinsic viscosity  $[\eta]$  of 1.8 dl/g, the melt tension of this olefin polymer is not less than 2.5 g, preferably not less than 3.5 g, more preferably not less than 4.0 g, much more preferably not less than 4.5 g, most preferably not less than 5.0 g.

The melt tension can be determined in the following manner.

Using a MT measuring machine (produced by Toyo Seiki Seisakusho K.K.), 7 g of a polymer is introduced into a cylinder having an orifice on the bottom and a piston, the cylinder being kept at a melting temperature of the polymer (polyethylene:  $190^{\circ}\text{C}$ ). After 5 minutes, the piston is pushed down at a rate of 10 mm/min. to extrude a molten polymer in the form of strand from the cylinder through the orifice provided on the bottom of the cylinder. The extruded strand is drawn in the form of filament, and wound up at a rate of 25 m/min. by way of a pulley of a load detector. In this stage, a stress applied to the pulley is measured. The obtained value is a melt tension of the polymer.

Next, the transition metal compound catalyst component [A] used for preparing the above-described  $\alpha$ -olefin/polyene copolymer-containing polymer [I] will be described.

The transition metal compound catalyst component [A] used in the invention is a compound containing a transition metal selected from metals in Group III to Group VIII of a periodic table, and preferably is a compound containing at least one transition metal selected from Ti, Zr, Hf, Nb, Ta, Cr and V.

Examples of such transition metal compound catalyst component [A] include a variety of known catalyst components, and concretely are solid titanium catalyst components containing titanium and halogen. In more concrete, one example of the solid titanium catalyst components is a solid titanium catalyst component [A-1] containing titanium, magnesium and halogen, and further containing an electron donor (a) if necessary.

Processes for preparing the solid titanium catalyst component [A-1] are described in detail in the following publications.

That is, the processes are described, for example, in Japanese Patent Publications No. 46(1971)-34092, No. 53(1978)-46799, No. 60(1985)-3323 and No. 63(1988)-54289, Japanese Patent Laid-open Publications No. 1(1989)-261404 and No. 1(1989)-261407, Japanese Patent Publications No. 47(1972)-41676, No. 47(1972)-46269 and No. 48(1973)-19794, Japanese Patent Laid-open Publications No. 60(1985)-262803, No. 59(1984)-147004, No. 59(1984)-149911, No. 1(1989)-201308, No. 61(1986)-151211, No. 53(1978)-58495, No. 53(1978)-87990, No.

59(1984)-206413, No. 58(1983)-206613, No. 58(1983)-125706, No. 63(1988)-68606, No. 63 (1988)-69806, No. 60(1985)-81210, No. 61(1986)-40306, No. 51(1976)-281189, No. 50(1975)-126590 and No. 51(1976)-92885, Japanese Patent Publications No. 57(1982)-45244, No.

57(1982)-26613 and No. 61(1986)-5483, Japanese Patent Laid-open Publication No. 56(1981)-811, Japanese Patent Publications No. 60(1985)-37804 and No. 59(1984)-50246, Japanese Patent Laid-open Publications No. 58(1983)-83006, No. 48(1973)-16986, No. 49(1974)-65999 and No.

20 49(1974)-86482, Japanese Patent Publications No. 56(1981)-39767 and No. 56(1981)-32322, and Japanese Patent Laid-open Publications No. 55(1980)-29591, No. 53(1978)-146292, No. 57(1982)-63310, No. 57(1982)-

63311, No. 57(1982)-63312, No. 62(1987)-273206, No. 63(1988)-69804, No. 61(1986)-21109, No. 63(1988)-264607, No. 60(1985)-23404, No. 60(1985)-44507, No.

30 60(1985)-158204, No. 61(1986)-55104, No. 2(1990)-28201, No. 58(1983)-196210, No. 64(1989)-54005, No. 59(1984)-149905, No. 61(1986)-145206, No. 63(1988)-302, No.

35 63(1988)-225605, No. 64(1989)-69610, No. 1(1989)-168707, No. 62(1987)-104810, No. 62(1987)-104811, No. 62(1987)-104812 and No. 62(1987)-104813.

The solid titanium catalyst component [A-1] can be prepared by using for example a titanium compound, a magnesium compound and if desired an electron donor (a), and bringing them into contact with each other.

Examples of the titanium compounds employable for preparing the solid titanium catalyst component [A-1] include tetravalent titanium compounds and trivalent titanium compounds.

As the tetravalent titanium compounds, there can be mentioned compounds represented by the following formula:

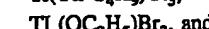
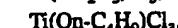


wherein R is a hydrocarbon group, X is a halogen atom, and g is a number satisfying the condition of  $0 \leq g \leq 4$ .

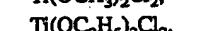
Concrete examples of such compounds are described below.

Titanium tetrahalides such as  $\text{TiCl}_4$ ,  $\text{TiBr}_4$ , and  $\text{TiI}_4$

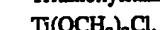
Alkoxytitanium trihalides such as:



Dialkoxytitanium dihalides such as:



Trialkoxytitanium monohalides such as:



ST AVAILABLE COPY



US005478922A

United States Patent [19]  
Rhee et al.

[11] Patent Number: 5,478,922  
[45] Date of Patent: Dec. 26, 1995

[54] PROCESS FOR POST REACTOR PURGING  
OF RESIDUAL MONOMERS FROM SOLID  
POLYMER RESINS

[75] Inventors: Aaron S. Rhee, Belle Mead; Duan-Fan  
Wang, Somerville, both of N.J.

[73] Assignee: Union Carbide Chemicals & Plastics  
Technology Corporation, Danbury,  
Conn.

[21] Appl. No.: 272,099

[22] Filed: Jul. 8, 1994

[51] Int. Cl. 6 C08F 6/28

[52] U.S. Cl. 528/483

[58] Field of Search 528/483

[56] References Cited

U.S. PATENT DOCUMENTS

3,450,183	6/1969	Hinton	159/2
3,594,356	7/1971	Hinton	260/88.2
4,197,399	4/1980	Noel et al.	528/500
4,372,758	2/1983	Bobst et al.	528/483
5,292,863	3/1994	Wang	528/483

FOREIGN PATENT DOCUMENTS

0059080 5/1986 European Pat. Off.

Primary Examiner—Joseph L. Shofer  
Assistant Examiner—Tom Weber  
Attorney, Agent, or Firm—B. L. Deppenbrock

[57] ABSTRACT

A process for removing unpolymerized monomers from a solid olefin polymer containing the monomers by counter-currently feeding an inert purge gas through a bed of polymer in a cylindrical purge vessel having tapered walls wherein the vessel has a height to bottom diameter ratio of 0.5:1 to 10:1 and the walls have a tapered angle based on a vertical axis of 0.5 to 15 degrees. An apparatus for removing unpolymerized monomers from a solid olefin polymer containing the monomers which comprises, a cylindrical purge vessel having tapered walls wherein the vessel has a height to bottom diameter ratio of 0.5:1 to 10:1 and the walls have a tapered angle based on a vertical axis of 0.5 to 15 degrees; a solids inlet disposed in an upper portion of the vessel; a solids discharge disposed in a lower portion of the vessel; gas entry means disposed within or below a bed of solids, and gas discharge means disposed in the upper portion of the vessel.

8 Claims, 1 Drawing Sheet

PROCESS FOR POST REACTOR PURGING  
OF RESIDUAL MONOMERS FROM SOLID  
POLYMER RESINS.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process and apparatus for removing unpolymerized monomers from solid olefin polymers. Particularly, the invention relates to a process for removing unpolymerized hydrocarbon monomers from a granular polymer of ethylene and/or propylene and one or more C<sub>4</sub> to C<sub>8</sub> alpha olefins. More particularly, the invention relates to a process for the removal of unpolymerized hydrocarbon monomers from "sticky polymers" such as ethylene propylene diene terpolymers.

2. Description of the Prior Art

It has long been known that olefins such as ethylene can be polymerized by contacting them under polymerization conditions with a catalyst comprising a transition metal compound, e.g., titanium tetrachloride and a cocatalyst or activator, e.g., an organometallic compound such a triethyl aluminum. Catalysts of this type are generally referred to as Ziegler catalysts.

The resulting granular polymers produced from these processes usually contain residual gaseous or liquid unpolymerized monomers including hydrocarbon monomers. These monomers should be removed from the granular resin for safety reasons, since there is a danger of explosion if the hydrocarbon monomer concentration becomes excessive in the presence of oxygen. In addition, proper disposal of the hydrocarbon is required in order to meet environmental standards concerning hydrocarbon emissions.

The prior art teaches techniques for removing volatile unpolymerized monomers from polymers of the corresponding monomers. See, for example, U.S. Pat. Nos. 4,197,399; 3,594,356, and 3,450,183, in which a columnar (or straight cylindrical) vessel is used as a purger.

U.S. Pat. No. 4,372,758, discloses a degassing or purging process for removing unpolymerized gaseous monomers from solid olefin polymers. The purging process generally comprises conveying the solid polymer (e.g., in granular form) to a column-shaped purge vessel and contacting the polymer in the purge vessel with a countercurrent inert gas purge stream to strip away the monomer gases which are evolved from the polymer. Purging efficiency of this countercurrent plug flow purger normally increases with the increase of the superficial velocity of the purge gas. However, if the gas velocity exceeds the minimum bubbling velocity (U<sub>mb</sub>) of the granular resin to be purged, the purger becomes a bubbling fluidized bed and there occur not only backmixing of purged and unpurged granular resin but also bypassing of purge gas, as bubbles, through the bed without having contact with the granular resin. These normally result in a substantially reduced purging efficiency for continuous mode operation of the purger. To avoid bubbling flow in the purger, therefore, the columnar purger is normally operated at a relatively low superficial gas velocity, below the minimum bubbling velocity of the resin. When the purger is operated at such low superficial gas velocities, however, the process tends to have uneven gas distribution in the purger. Purge gas seems to bypass through certain channels without contact with the majority of solids. This also results in a poor purging performance. This poor solid-gas contact phenomena in the conventional packed bed process may be one reason why actual purging is at least one order of magnitude

worse than theoretical predictions.

Further, when producing certain types of ethylene polymers, such as ethylene propylene diene terpolymers and "sticky polymers", monomers such as ethylidene norbornene (ENB) remaining in the product must be substantially purged from the product due to cost and environmental considerations. However ENB has a significantly low diffusivity as compared to other monomers. If a conventional columnar packed bed process is used, it would require an impractically long residence time or an extra large amount of purge gas. It is clear that such a process is not entirely suitable for ENB purging.

U.S. Pat. No. 5,292,863, ameliorates this problem by providing a process for removing unpolymerized gaseous monomers from a solid olefin polymer by utilizing a column-shaped purge vessel provided with a gas permeable, solids impermeable constraint means. An inert feed gas is fed to the purge vessel and in countercurrent contact with the polymer, the inert purge gas being utilized in an amount and at a velocity sufficient to form a fully expanded bed in the purge vessel. Although this process overcomes many disadvantages incident to prior art techniques, it is not the simplest process, since the process requires the use of a gas permeable, solids impermeable constraint means to confine solids and suppress bubbling fluidization.

Accordingly, there is a need for a more effective process and apparatus for purging solid olefin polymers. Surprisingly, the present invention is an improvement over existing systems because it affords greater latitude in adjusting or regulating the superficial gas velocity to result in more efficient purging in less time without the use of a gas permeable, solids impermeable constraint means. The process and apparatus of the present invention more effectively provides that individual solid particles in the bed of the purge vessel will be swept by the purge gas and thus offer improved solid-gas contact.

SUMMARY OF THE INVENTION

The present invention provides a process for removing unpolymerized hydrocarbon monomers from a solid olefin polymer which comprises:

- (a) countercurrently passing a purge gas through a bed of polymer in a cylindrical purge vessel having tapered walls wherein the vessel has a height to bottom diameter ratio of 0.5:1 to 10:1 and the walls have a tapered angle based on a vertical axis of 0.5 to 15 degrees;
- (b) discharging the gaseous stream containing the monomer out of the vessel; and
- (c) discharging polymer solids from the vessel.

The present invention also provides an apparatus for removing unpolymerized hydrocarbon monomers from a solid olefin polymer containing the monomers which comprises, a cylindrical purge vessel having tapered walls wherein the vessel has a height to bottom diameter ratio of 0.5:1 to 10:1 and the walls have a tapered angle based on a vertical axis of 0.5 to 15 degrees; a solids inlet disposed in an upper portion of the vessel; a solids discharge disposed in a lower portion of the vessel; gas entry means disposed within or below a bed of solids, and gas discharge means disposed in the upper portion of the vessel.

In a preferred aspect, the process and apparatus of the present invention is directed to the purging of ethylene propylene diene monomer (EPDM) resin to reduce the amount of residual diene monomer such as ethylidene norbornene (ENB) present in the resin.

#### BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a representation of a preferred purge vessel system of the present invention with certain parts broken away to reveal interior details. In FIG. 1, 1 is an inlet conduit for solid polymer entering the vessel for purging; 2 is the discharge end; 3 is a gas distributor plate; 4 is a plurality of tubes in the distributor plate; 5 is a conduit for entering purge gas; 6 is a discharge conduit for purged polymer resin; 7 is a rotary valve; 8 is an inverted truncated cone shaped transition element; 9 is the tapered wall of the vessel; 10 is a cylindrical vessel having tapered walls; and 11 is a conduit for the exiting purge gas conveying the residual monomer.

## DETAILED DESCRIPTION OF THE INVENTION

Polymers

The solid olefin polymers to be purged can be produced by a variety of well known techniques. A particularly preferred technique is to produce the solid olefin polymers by a gas phase fluidized bed process which utilizes a fluid bed reactor such as described in U.S. Pat. No. 4,482,687.

Solid olefin polymers which can be purged using the process and apparatus of the present invention are preferably granular. They can include polyolefins or alpha olefins such as, for example, homopolymers of ethylene or propylene; 25 copolymers and terpolymers of a major mole percent of ethylene and/or propylene as the main monomer(s) and a minor mole percent of ~~one or more C<sub>3</sub> to C<sub>8</sub> olefins~~ <sup>30</sup> sticky polymer, as well as polyvinyl chlorides; and elastomers such as polybutadiene, EPMS, and EPDMs. The preferred ~~C<sub>3</sub> to C<sub>8</sub> alpha olefins are propylene, butene, pentene, 1,4-pentadiene, 1,6-pentene, and octene-1.~~ <sup>35</sup> This description is not intended to exclude the use of this invention with alpha olefin monomers, copolymer resins in which ethylene is not a monomer. Examples of sticky polymers which can be benefited by the present invention include ethylene/propylene rubbers and ethylene/propylene/diene rubbers, polybutadiene rubbers, high ethylene content propylene/ethylene block copolymers, poly(1-butene) (when produced under certain reaction conditions), very low density (low modulus) polyethylenes, i.e., ethylene/butene rubbers or hexene containing terpolymers, ethylene/propylene/ethylidene norbornene and ethylene/propylene/hexadiene terpolymers of low density. <sup>40</sup>

For purposes of ease of description only, the present invention will be described herein with particular reference to EPDM terpolymers where applicable, although it is to be expressly understood that the invention is not to be limited thereby. Rather, it is the intention to be limited only by the scope of the claims appended hereto. The invention is preferably practiced with sticky polymers which have been rendered "non-sticky" such as by the process disclosed in U.S. Pat. No. 4,994,534, issued Feb. 19, 1991.

Depending upon the conditions of reaction and the particular diene monomer, the resulting EPDM terpolymer can contain an amount of liquid and/or gaseous unpolymerized hydrocarbon monomers, (which may include ethylene, propylene, and, e.g., ethylidene norbornene). The process and apparatus of the present invention is especially useful for purging higher boiling or liquid monomers such as ethylidene norbornene.

Environmental restrictions may prevent the direct venting to the atmosphere of such residual monomers and more importantly, health and safety considerations generally require that these materials be substantially removed from the solid polymer. The present invention may be employed to accomplish these desired objectives.

### Operation of the Purging Process

The process of the present invention is believed to involve only a physical process i.e., the monomers are only entrained or otherwise contained within and between the resin particles and diffuse out into a countercurrent gas purge stream. The diffusion of the monomers into the purge gas occurs until an equilibrium is established between the monomer concentration in the resin and in the purge gas. A large difference between monomer concentrations in the resin and in the purge stream obviously favors a high rate of diffusion. In addition, the rate of diffusion is dependent to a degree upon the temperature and pressure within the purge vessel, with higher temperatures favoring higher diffusion rates and therefore lower residence times in the purge vessel and with lower pressures also favoring higher rates of diffusion. The rate of diffusion also depends on the resin particle size and particle morphology, with the rate being higher for smaller particle sizes. Therefore, depending upon the initial monomer concentration in the resin and the final concentration desired, the residence time of the resin in the purge vessel can be determined using known mass transfer techniques based on the resin temperature, particle size distribution and morphology, rate of flow of purge gas, the pressure in the purge vessel, and the size of the purge vessel. In general for EPDM materials, when processing a particle size of about 0.025 inches average particle size having a temperature of about 60° C. and at a purge gas velocity of about 0.5 ft/second, a residence time on the order of about three hours is generally preferred to reduce the monomer concentration to a safe and environmentally acceptable value. It is preferred to feed to the purge vessel a purge gas which contains as little as possible or no hydrocarbons. Of course, economic considerations also affect the design of the purge vessel. Those skilled in the art will be able to practice the present invention based upon the more detailed discussions contained herein, and using standard chemical engineering techniques.

FIG. 1 illustrates a preferred embodiment of the process of the invention. Referring to FIG. 1, a cylindrical purge vessel 10 is shown which is provided with an entry means such as inlet conduit 1 for a solid polymer (resin) which must be purged and which is introduced into the vessel by gravity. Alternatively, the resin can be introduced into the purge vessel using a conveying gas such as nitrogen. The cylindrical purge vessel has tapered walls 9. The height to bottom diameter ratio of the vessel is 0.5:1 to 10:1, preferably 1.5:1 to 8:1, and most preferably is 4:1 to 7:1. The vessel has tapered or angled walls 9 to accommodate a bed of solids. The cross-sectional area of the vessel increases from the bottom to the top. The angle of the walls 9 is dependent upon the size of polymers to be purged and the amount of purge gas to be used. In general practices, the tapered angle as measured along the vertical axis of the vessel can range from 0.5 to 15 degrees, and preferably is 3 to 10 degrees.

The purge gas, preferably an inert purge gas is introduced into the vessel at its lower end through conduit 5 and is directed through a gas distributing means such as distributor plate 3 which serves to provide uniform purge gas distribution. The gas distributor of choice should allow the solids to be discharged from the bottom of the bed and thus enable the solid bed to be operated in a counter-current mode. As shown in FIG. 1, distributor 3 is positioned at the base of the purge vessel in communication with conduit 5 and at a point slightly above a transition element 8. The transition element has an inverted truncated conical shape and connects the tapered purge vessel to the rotary valve 6. As known to those